PATENT COOPERATION TREATY

PCT

INTERNATIONAL SEARCH REPORT

(PCT Article 18 and Rules 43 and 44)

Applicant's or agent's file reference	**FOR FURTHER ACTION** see Notification of Transmittal of International Search Report (Form PCT/ISA/220) as well as, where applicable, item 5 below.	
RM/X89634/PC		
International application No.	International filing date *(day/month/year)*	(Earliest) Priority Date *(day/month/year)*
PCT/IT 00/ 00229	05/06/2000	03/06/1999
Applicant		
CONSIGLIO NAZIONALE DELLE RICERCHE et al.		

This International Search Report has been prepared by this International Searching Authority and is transmitted to the applicant according to Article 18. A copy is being transmitted to the International Bureau.

This International Search Report consists of a total of 4 sheets.

[X] It is also accompanied by a copy of each prior art document cited in this report.

1. **Basis of the report**

   a. With regard to the **language,** the international search was carried out on the basis of the international application in the language in which it was filed, unless otherwise indicated under this item.

   [ ] the international search was carried out on the basis of a translation of the international application furnished to this Authority (Rule 23.1(b)).

   b. With regard to any **nucleotide and/or amino acid sequence** disclosed in the international application, the international search was carried out on the basis of the sequence listing :

   [ ] contained in the international application in written form.

   [ ] filed together with the international application in computer readable form.

   [ ] furnished subsequently to this Authority in written form.

   [ ] furnished subsequently to this Authority in computer readble form.

   [ ] the statement that the subsequently furnished written sequence listing does not go beyond the disclosure in the international application as filed has been furnished.

   [ ] the statement that the information recorded in computer readable form is identical to the written sequence listing has been furnished

2. [ ] **Certain claims were found unsearchable** (See Box I).

3. [ ] **Unity of invention is lacking** (see Box II).

4. With regard to the **title,**

   [X] the text is approved as submitted by the applicant.

   [ ] the text has been established by this Authority to read as follows:

5. With regard to the **abstract,**

   [ ] the text is approved as submitted by the applicant.

   [X] th t xt has been established, according to Rule 38.2(b), by this Authority as it appears in Box III. The applicant may, within on month from th date of mailing of this international search report, submit comments to this Authority.

6. Th figure of th **drawings** to b publish d with th abstract is Figure No. 1

   [X] as suggested by th applicant.

   [ ] because the applicant failed to suggest a figure.

   [ ] because this figure better characterizes the invention.

   [ ] Non of th figures.

B x III TEXT OF THE ABSTRACT (Continuation of item 5 of the first sheet)

The abstract has to be changed as follows:

Line 2, after "electrode" insert "(14)";
line 3, after "electrode" insert "(15)", after "electrolyte" insert "(S)";
line 5, after "aperture" insert "(19)";
line 6, after "environment" insert "(E)";
line 7, after "means" insert "(A)".

INTERNATIONAL SEARCH REPORT

International Application No
P[redacted]T 00/00229

A. CLASSIFICATION OF SUBJECT MATTER
IPC 7 H01M2/10 H01M2/12 H01M10/42 H01M6/34

According to International Patent Classification (IPC) or to both national classification and IPC

B. FIELDS SEARCHED

Minimum documentation searched (classification system followed by classification symbols)
IPC 7 H01M

Documentation searched other than minimum documentation to the extent that such documents are included in the fields searched

Electronic data base consulted during the international search (name of data base and, where practical, search terms used)
EPO-Internal, WPI Data, PAJ

C. DOCUMENTS CONSIDERED TO BE RELEVANT

Category °	Citation of document, with indication, where appropriate, of the relevant passages	Relevant to claim No.
A	US 3 925 592 A (WEBB ALAN DAVID) 9 December 1975 (1975-12-09) figure 1 column 1, line 22 - line 34 column 1, line 52 - line 55 column 1, line 65 -column 2, line 6 column 2, line 27 - line 41 column 2, line 55 -column 3, line 18 --- -/--	1,3,5,7, 9,10

[X] Further documents are listed in the continuation of box C.

[X] Patent family members are listed in annex.

° Special categories of cited documents :

"A" document defining the general state of the art which is not considered to be of particular relevance

"E" earlier document but published on or after the international filing date

"L" document which may throw doubts on priority claim(s) or which is cited to establish the publication date of another citation or other special reason (as specified)

"O" document referring to an oral disclosure, use, exhibition or other means

"P" document published prior to the international filing date but later than the priority date claimed

"T" later document published after the international filing date or priority date and not in conflict with the application but cited to understand the principle or theory underlying the invention

"X" document of particular relevance; the claimed invention cannot be considered novel or cannot be considered to involve an inventive step when the document is taken alone

"Y" document of particular relevance; the claimed invention cannot be considered to involve an inventive step when the document is combined with one or more other such documents, such combination being obvious to a person skilled in the art.

"&" document member of the same patent family

Date of the actual completion of the international search	Date of mailing of the international search report
10 October 2000	17/10/2000

Name and mailing address of the ISA	Authorized officer
European Patent Office, P.B. 5818 Patentlaan 2 NL – 2280 HV Rijswijk Tel. (+31–70) 340–2040, Tx. 31 651 epo nl, Fax: (+31–70) 340–3016	Gamez, A

1

Form PCT/ISA/210 (second sheet) (July 1992)

INTERNATIONAL SEARCH REPORT

International Application No
P[redacted]T 00/00229

C.(Continuation) DOCUMENTS CONSIDERED TO BE RELEVANT

Category °	Citation of document, with indication,where appropriate, of the relevant passages	Relevant to claim No.
A	US 5 876 872 A (FEEZOR MICHAEL D) 2 March 1999 (1999-03-02) figures 3,6 column 3, line 56 -column 4, line 7 column 5, line 1 - line 22 column 5, line 35 -column 6, line 46 table 1 column 9, line 44 - line 53 column 10, line 26 - line 35 column 11, line 1 - line 18	1,2,5,6, 10
A	US 3 553 018 A (DANIELS EARL L JR ET AL) 5 January 1971 (1971-01-05) column 1, line 15 - line 25 column 2, line 40 - line 34	1,3,7, 9-11
A	US 3 589 940 A (BRIDGE LAURENCE ET AL) 29 June 1971 (1971-06-29) figure 1 column 2, line 68 -column 3, line 9 column 3, line 40 -column 4, line 6	1,7,11

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INTERNATIONAL SEARCH REPORT

Info on patent family members

International Application No
P[redacted]T 00/00229

Patent document cited in search report	Publication dat	Patent family member(s)	Publication date
US 3925592 A	09-12-1975	GB 1463662 A FR 2221898 A	02-02-1977 11-10-1974
US 5876872 A	02-03-1999	NONE	
US 3553018 A	05-01-1971	NONE	
US 3589940 A	29-06-1971	US 3544372 A	01-12-1970

PATENT COOPERATION TREATY

From the INTERNATIONAL BUREAU

PCT

NOTIFICATION OF ELECTION

(PCT Rule 61.2)

To:

Commissioner
US Department of Commerce
United States Patent and Trademark
Office, PCT
2011 South Clark Place Room
CP2/5C24
Arlington, VA 22202
ETATS-UNIS D'AMERIQUE

in its capacity as elected Office

Date of mailing (day/month/year) 08 February 2001 (08.02.01)	
International application No. PCT/IT00/00229	**Applicant's or agent's file reference** RM/X89634/PC
International filing date (day/month/year) 05 June 2000 (05.06.00)	**Priority date** (day/month/year) 03 June 1999 (03.06.99)
Applicant ZOCCHI, Fernando	

1. The designated Office is hereby notified of its election made:

[X] in the demand filed with the International Preliminary Examining Authority on:

18 December 2000 (18.12.00)

[ ] in a notice effecting later election filed with the International Bureau on:

2. The election [X] was

[ ] was not

made before the expiration of 19 months from the priority date or, where Rule 32 applies, within the time limit under Rule 32.2(b).

The International Bureau of WIPO **34, chemin des Colombettes** **1211 Geneva 20, Switzerland**	Authorized officer Zakaria EL KHODARY
Facsimile No.: (41-22) 740.14.35	Telephone No.: (41-22) 338.83.38

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PATENT COOPERATION TREATY

REC'D 12 SEP 2001
WIPO PCT

PCT

INTERNATIONAL PRELIMINARY EXAMINATION REPORT

(PCT Article 36 and Rule 70)

Applicant's or agent's file reference	FOR FURTHER ACTION	See Notification of Transmittal of International Preliminary Examination Report (Form PCT/IPEA/416)
./.		
International application No.	International filing date *(day/month/year)*	Priority date *(day/month/year)*
PCT/IT00/00229	05/06/2000	03/06/1999
International Patent Classification (IPC) or national classification and IPC H01M2/10		
Applicant CONSIGLIO NAZIONALE DELLE RICERCHE et al.		

1. This international preliminary examination report has been prepared by this International Preliminary Examining Authority and is transmitted to the applicant according to Article 36.

2. This REPORT consists of a total of 6 sheets, including this cover sheet.

   ☒ This report is also accompanied by ANNEXES, i.e. sheets of the description, claims and/or drawings which have been amended and are the basis for this report and/or sheets containing rectifications made before this Authority (see Rule 70.16 and Section 607 of the Administrative Instructions under the PCT).

   These annexes consist of a total of 1 sheets.

3. This report contains indications relating to the following items:

   - I ☒ Basis of the report
   - II ☐ Priority
   - III ☐ Non-establishment of opinion with regard to novelty, inventive step and industrial applicability
   - IV ☐ Lack of unity of invention
   - V ☒ Reasoned statement under Article 35(2) with regard to novelty, inventive step or industrial applicability; citations and explanations suporting such statement
   - VI ☐ Certain documents cited
   - VII ☒ Certain defects in the international application
   - VIII ☒ Certain observations on the international application

Date of submission of the demand	Date of completion of this report
18/12/2000	10.09.2001
Name and mailing address of the international preliminary examining authority: European Patent Office D-80298 Munich Tel. +49 89 2399 - 0 Tx: 523656 epmu d Fax: +49 89 2399 - 4465	Authorized officer Fitzpatrick, J Telephone No. +49 89 2399 8570

Form PCT/IPEA/409 (cover sheet) (January 1994)

INTERNATIONAL PRELIMINARY EXAMINATION REPORT

International application No. PCT/IT00/00229

I. Basis of the report

1. With regard to the **elements** of the international application *(Replacement sheets which have been furnished to the receiving Office in response to an invitation under Article 14 are referred to in this report as "originally filed" and are not annexed to this report since they do not contain amendments (Rules 70.16 and 70.17))*:
Description, pages:

1-10	as originally filed				

Claims, No.:

1-5	as received on	16/07/2001	with letter of	13/07/2001	

Drawings, sheets:

1/7-7/7	as originally filed				

2. With regard to the **language**, all the elements marked above were available or furnished to this Authority in the language in which the international application was filed, unless otherwise indicated under this item.

   These elements were available or furnished to this Authority in the following language: , which is:

   - ☐ the language of a translation furnished for the purposes of the international search (under Rule 23.1(b)).
   - ☐ the language of publication of the international application (under Rule 48.3(b)).
   - ☐ the language of a translation furnished for the purposes of international preliminary examination (under Rule 55.2 and/or 55.3).

3. With regard to any **nucleotide and/or amino acid sequence** disclosed in the international application, the international preliminary examination was carried out on the basis of the sequence listing:

   - ☐ contained in the international application in written form.
   - ☐ filed together with the international application in computer readable form.
   - ☐ furnished subsequently to this Authority in written form.
   - ☐ furnished subsequently to this Authority in computer readable form.
   - ☐ The statement that the subsequently furnished written sequence listing does not go beyond the disclosure in the international application as filed has been furnished.
   - ☐ The statement that the information recorded ~~in computer~~ readable form is identical to the written sequence listing has been furnished.

4. The amendments have resulted in the cancellation of:

   - ☐ the description, pages:
   - ☐ the claims, Nos.:

☐ the drawings, sheets:

5. ☒ This report has been established as if (some of) the amendments had not been made, since they have been considered to go beyond the disclosure as filed (Rule 70.2(c)):

   (Any replacement sheet containing such amendments must be referred to under item 1 and annexed to this report.)
   see separate sheet

6. Additional observations, if necessary:

V. Reasoned statement under Article 35(2) with regard to novelty, inventive step or industrial applicability; citations and explanations supporting such statement

1. Statement

Novelty (N)	Yes:	Claims	1-5
	No:	Claims	
Inventive step (IS)	Yes:	Claims	1-5
	No:	Claims	
Industrial applicability (IA)	Yes:	Claims	1-5
	No:	Claims	

2. Citations and explanations
   see separate sheet

VII. Certain defects in the international application

The following defects in the form or contents of the international application have been noted:
see separate sheet

VIII. Certain observations on the international application

The following observations on the clarity of the claims, description, and drawings or on the question whether the claims are fully supported by the description, are made:
see separate sheet

Section I

I.5: Amendments

Whilst the individual liquid separating means of new claim 1 are disclosed in original claim 6 and on original page 8, the suggestion of mixtures/admixtures on said page 8, lines 34-35 is only a general one and provides no acceptable basis for the selection of the specific admixture now claimed. Moreover, line 35 on page 8 provides only a basis for an admixture with hydrocarbons. For either of these reasons, the "admixtures" amendment to claim 1 infringes Art.34(2)(b) PCT and is thus not allowable.

Despite the generalisation to "lead acid" in claim 1 covering acids other than the disclosed sulphuric acid of pages 1 and 9, the general references to any acid particularly in the first paragraph on page 8 are just sufficient when read in the context of the application to render said generalisation as acceptable under Art.34(2)(b) PCT.

Section V.2: Citations and Explanations

(i) The prior art documents of the International Search Report (ISR) can be summarised as follows:

US 3 925 592 (D1)

With particular reference to Figure 1 thereof, disclosed are battery cell elements (such as the twenty Ni-Cd cells filled with caustic potash electrolyte of col.2, lines 55-57) connected in series such as to form battery 11 for use underwater. The battery is held in container 2, which container has cover 6 and which container is fully filled with a lighter than water non-electrically conducting oil such that oil is allowed to overflow through the vent hole in the top of the cover 6 before the plug 9 is inserted. Each of the battery cell elements has a vent 21 which is open as it allows the oil in container 2 to enter the cells and fill the spaces above the electrolyte. In view of the double wall (3,4) and annular space 5 design of the container, an opening exists at the side of the container which forms an interface between the internal oil and the external water environment. The oil thus constitutes a liquid separating means between the electrolyte and the external water. Moreover, the open vent 21 of each cell unit constitute apertures which communicates via the intervening oil (as in the embodiment of Fig. 4 of the current application) with the external water environment through this side opening.

The vents 21 allow the escape of gases produced from the battery and being filled with oil, they also prevent the external liquid (sea water) from entering the battery.

US 5 876 872 (D2)

With particular reference to Fig. 5 thereof, whereby here the pressure relief valves 42 are the apertures which communicate with the external sea water via the pressure compensating fluid 84 and the pressure relief valve 94 and vent 96. Here again, said fluid in combination with said valves 94 and 96 separates the electrolyte from the sea water. In this respect, the wording of current claim 1 does not preclude the presence of additional separating means such as these valves. Thus claim 1 only refers to the "**liquid** separating means ..... consisting of .... ". That this is so is moreover confirmed in the embodiments of current Figs 2-4 which all have "solid" additional features between the liquid separating means and the external water. Fig. 4 of the current application is indeed very similar to Fig.5 of D2. That the cells of Fig.5 must be connected in series is clear in view of the power requirements of the systems referred to in D2. This is moreover confirmed in Fig. 7 of D2. The pressure compensation fluid used in D2 includes those intermediate in density between the cell electrolyte and the external sea/fresh water and include the chlorinated hydrocarbons. D2 at col.3, lines 64-66 also anticipates using the batteries in fresh water.

US 3 553 018 (D3) and US 3 589 940 (D4)

Both these closely related documents are also more relevant than suggested in the ISR and with particular reference to the specific citations of the ISR, have in common with the current invention that they disclose underwater batteries containing vented cells whereby the electrolyte is separated from the external environment via electrically non-conductive liquid such as oil and whereby the vents communicate with the external environment via the oil and additional vents in the outer housing of the batteries.

(ii) The closest prior art can be considered to be that of document D2 which discloses a battery which contains a pressure compensation fluid 84 serving the same purpose as the liquid separating means of the present invention and which fluid has density preferably intermediate between the density of the external seawater and that of the electrolyte. For the case of Pb/acid batteries however document D2 indicates that the density of sulphuric acid in a Pb acid battery varies from about 1.2 to 1.3 g/cm^3 for a fully charged battery to 1.1g/cm^3 or less for a discharged battery. . Consequently it is

concluded that such intermediate density pressure compensating fluids are not suitable since "they are not reliably high enough to ensure separation from an ambient water by a fluid of intermediate density" (see D2, col.9, first paragraph). This follows in that whilst the density of water is 0.9998 g/cm^3, the density of seawater is between 1.02 and 1.04 g/cm^3 (D2, col.5, lines 15-17). This thus presents a technical prejudice to the use of fluids with such intermediate densities in conventional Pb acid batteries. Indeed, from col. 9, lines 6-11, document D2 only makes such use possible by substantially increasing the concentration and density of the Pb acid electrolyte to 50% or more (density = 1.4 g/cm^3). This however apparently leads to deep sulphation (coating with $PbSO_4$) of the electrodes and a rapid decrease in efficiency. The current Applicant's have however indicated that the specific claimed liquid separating fluids, which are no where disclosed in the available prior art of the Search Report, facilitate effective electrolyte-seawater separation whilst still allowing pressure compensation and thus overcome the technical prejudice. This is not only attributed to their intermediate densities (1-bromodecane = 1.069; Silicon oil Dow Corning 710 = 1.103) but also to their lower degree of molecule polarisation and longer carbon chain rendering them even less soluble than, for example, the chlorinated hydrocarbons disclosed in D2. Their very low solubilities and low vapour pressure apparently also have the effect that these two fluids have a lower environmental impact. The requirements of Art.33(2)-(4) PCT are thus considered to be adequately fulfilled.

Section VII: Certain Defects

Contrary to the requirements of Rule 5.1(a)(ii) PCT, the relevant background art disclosed in the documents D1-D4 was not mentioned in the description, nor were these documents identified therein.

Section VIII: Certain Observations under Art.6 PCT

(i) The description has not been adapted to the new claims. The scope of the invention is thus rendered unclear via the different scope of the invention apparent from the numerous conflicting embodiments of the description.

(ii) Claim 4 should have read "through-leads".

PATENT COOPERATION TREATY

From the
INTERNATIONAL PRELIMINARY EXAMINING AUTHORITY

To:

BORRINI, Stefano
Societa Italiana Brevetti S.p.A.
39 Piazza di Pietra
00186 Roma
ITALIE

RICEVUTO
13 SET. 2001
SOCIETA' ITALIANA BREVETTI S.p.A.
Piazza di Pietra, 39
00186 ROMA

PCT

NOTIFICATION OF TRANSMITTAL OF THE INTERNATIONAL PRELIMINARY EXAMINATION REPORT
(PCT Rule 71.1)

Date of mailing *(day/month/year)*	10.09.2001
Applicant's or agent's file reference ./.	**IMPORTANT NOTIFICATION**

International application No.	International filing date *(day/month/year)*	Priority date *(day/month/year)*
PCT/IT00/00229	05/06/2000	03/06/1999

Applicant
CONSIGLIO NAZIONALE DELLE RICERCHE et al.

1. The applicant is hereby notified that this International Preliminary Examining Authority transmits herewith the international preliminary examination report and its annexes, if any, established on the international application.

2. A copy of the report and its annexes, if any, is being transmitted to the International Bureau for communication to all the elected Offices.

3. Where required by any of the elected Offices, the International Bureau will prepare an English translation of the report (but not of any annexes) and will transmit such translation to those Offices.

4. **REMINDER**

The applicant must enter the national phase before each elected Office by performing certain acts (filing translations and paying national fees) within 30 months from the priority date (or later in some Offices) (Article 39(1)) (see also the reminder sent by the International Bureau with Form PCT/IB/301).

Where a translation of the international application must be furnished to an elected Office, that translation must contain a translation of any annexes to the international preliminary examination report. It is the applicant's responsibility to prepare and furnish such translation directly to each elected Office concerned.

For further details on the applicable time limits and requirements of the elected Offices, see Volume II of the PCT Applicant's Guide.

Name and mailing address of the IPEA/	Authorized officer
European Patent Office D-80298 Munich Tel. +49 89 2399 - 0 Tx: 523656 epmu d Fax: +49 89 2399 - 4465	Krage, D Tel.+49 89 2399-7530

CLAIMS

1. A lead acid battery for underwater use comprising a plurality of series connected elements contained in a casing, each element having a positive electrode and a negative electrode in a liquid electrolyte, each element being provided with an aperture communicating with the external environment,

liquid separating means provided in contact with the electrolyte, consisting of a liquid that is non-ionised, insoluble and non-reactive both in respect of said electrolyte and of the external liquid environment made of fresh or salty water

characterised by the fact that said liquid separating means belong to the class formed by 1-bromodecane, silicone oil with density equivalent to Dow Corning DC 710 and their admixtures.

2. The battery according to claim 1, wherein said elements are made of cell units.

3. The battery according to claim 1 or 2, wherein each element or cell unit is provided with an individual communication element comprising an expansion chamber delimited by chokes.

4. The battery according to one or more of the preceding claims, wherein insulated and liquid-tight thorough-leads for connecting said battery to an electric load or to a battery recharger are provided.

5. The battery according to one or more of the preceding claims, wherein said elements or cell units are of the lead/sulphuric acid type.

CLAIMS

1. A battery for underwater use comprising a plurality of elements, each having a positive electrode and a negative electrode in a liquid electrolyte, characterised in that said elements are series connected and in that each element is provided with an aperture communicating with the external liquid environment, and in that liquid separating means are provided between the electrolyte and the external liquid environment, consisting of a liquid that is non-ionised, insoluble and non-reactive both in respect of said electrolyte and in respect of said external liquid environment.

2. The battery according to claim 1, characterised in that said elements are made of cell units and in that said liquid separating means have a density intermediate between that of said electrolyte and that of the external liquid means, made of fresh or salty water.

3. The battery according to claim 1 or 2, characterised in that at the top of each element or cell unit an aperture communicating with the external liquid environment is provided in order to allow a hydrostatic pressure balancing between the interior and the exterior of the battery, said aperture being chamber-shaped and vented at the top thereof, and with one or more narrow openings in order to avoid the leaking toward the external environment of the liquid separating means and of the electrolyte when said battery is tilted.

4. The battery according to one or more of the claims 1 to 3, characterised in that said apertures at the top of each element or cell unit are connected to a manifold having an individual aperture in correspondence of the external environment.

5. The battery according to one or more of the preceding claims, characterised in that it comprises a secondary casing housing said battery, wherein the space between the battery and said casing is filled up with said liquid separating means and it is provided with an

individual aperture communicating with the external environment, there being also provided insulated and liquid-tight thorough-leads for connecting said battery to an electric load or to a battery recharger.

6. The battery according to one or more of the preceding claims, characterised in that said liquid separating means which are non-ionised and non-reactive with the electrolyte of the battery and with the external liquid environment and have an intermediate density between that of the battery electrolyte and that of the external liquid environment, consisting of fresh or salt water, are selected from one or more of the following substance classes:

chlorinated hydrocarbons, like, e.g., 1,1,1-trichloroethane, chlorobenzene, 1,1,2,2-tetrachloroethane, 1,2-dichlorobenzene, carbon tetrachloride, trichloroethylene, 2-chlorotoluene, 4-chlorotoluene;

bromidrated hydrocarbons, like, e.g., 1-bromodecane, bromobenzene, 1-bromohexane, bromocyclohexane;

nitroderivatives of hydrocarbons, like, e.g., nitrobenzene;

silicones, like, e.g., the silicone oil 710.

7. The battery according to claim 1, characterised in that said elements are made of cell units and in that said liquid separating means have a density that is lower than that of the electrolyte, and in that at the top of each element or cell unit a check valve is provided, arranged so as to allow the escape of gases produced during the operation of the battery and to prevent the entering of the external liquid environment.

8. The battery according to claim 7, characterised in that said apertures at the top of each element or cell unit are connected to a manifold having a individual check valve.

9. The battery according to claim 7 and/or 8 characterised in that said liquid separating means have a

density that is lower than that of the electrolyte and also of the external liquid environment and consist of oil, naphtha, kerosene, mineral oil (Nujol), liquid paraffin and mixtures thereof.

10. The battery according to one or more of the preceding claims, characterised in that said elements or cell units are of the lead/sulphoric acid type or the nickel-iron or nickel-cadmium type.

11. The battery according to one or more of the preceding claims, characterised in that, in the assemblies provided with check valves, the casing of the battery and/or said secondary casing are made of a relatively yielding material, in order to compensate the different compressibility between the external liquid means and the complex electrolyte/separating liquid.

(12) INTERNATIONAL APPLICATION PUBLISHED UNDER THE PATENT COOPERATION TREATY (PCT)

(19) World Intellectual Property Organization
International Bureau

(43) International Publication Date
14 December 2000 (14.12.2000)

PCT

(10) International Publication Number
WO 00/76013 A1

(51) International Patent Classification[7]: H01M 2/10, 2/12, 10/42, 6/34

(21) International Application Number: PCT/IT00/00229

(22) International Filing Date: 5 June 2000 (05.06.2000)

(25) Filing Language: English

(26) Publication Language: English

(30) Priority Data:
RM99A000355 3 June 1999 (03.06.1999) IT

(71) Applicants *(for all designated States except US)*: **CONSIGLIO NAZIONALE DELLE RICERCHE** [IT/IT]; Piazzale Aldo Moro, 7, I-00185 Roma (IT). **A.L.A. ELETTRONICA S.R.L. also known as ALA ELETTRONICA S.R.L.** [IT/IT]; Via della Maggiona, 5, I-00040 Pomezia (IT).

(72) Inventor; and

(75) Inventor/Applicant *(for US only)*: **ZOCCHI, Fernando** [IT/IT]; Via Tommaso Arcidiacono, 119, sc A/6, I-00143 Roma (IT).

(74) Agents: **BORRINI, Stefano** et al.; Società Italiana Brevetti S.p.A., Piazza di Pietra, 39, I-00186 Roma (IT).

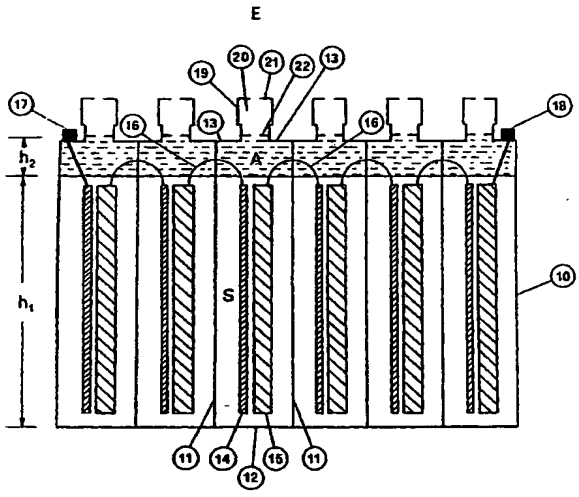
(81) Designated States *(national)*: AE, AG, AL, AM, AT, AU, AZ, BA, BB, BG, BR, BY, CA, CH, CN, CR, CU, CZ, DE, DK, DM, DZ, EE, ES, FI, GB, GD, GE, GH, GM, HR, HU, ID, IL, IN, IS, JP, KE, KG, KP, KR, KZ, LC, LK, LR, LS, LT, LU, LV, MA, MD, MG, MK, MN, MW, MX, MZ, NO, NZ, PL, PT, RO, RU, SD, SE, SG, SI, SK, SL, TJ, TM, TR, TT, TZ, UA, UG, US, UZ, VN, YU, ZA, ZW.

(84) Designated States *(regional)*: ARIPO patent (GH, GM, KE, LS, MW, MZ, SD, SL, SZ, TZ, UG, ZW), Eurasian patent (AM, AZ, BY, KG, KZ, MD, RU, TJ, TM), European patent (AT, BE, CH, CY, DE, DK, ES, FI, FR, GB, GR, IE, IT, LU, MC, NL, PT, SE), OAPI patent (BF, BJ, CF, CG, CI, CM, GA, GN, GW, ML, MR, NE, SN, TD, TG).

Published:
— *With international search report.*
— *Before the expiration of the time limit for amending the claims and to be republished in the event of receipt of amendments.*

For two-letter codes and other abbreviations, refer to the "Guidance Notes on Codes and Abbreviations" appearing at the beginning of each regular issue of the PCT Gazette.

(54) Title: UNDERWATER BATTERIES PROVIDED WITH LIQUID SEPARATING MEANS BETWEEN INTERNAL ELECTROCHEMICAL ENVIRONMENT AND EXTERNAL LIQUID ENVIRONMENT



(57) Abstract: A battery for underwater use comprising a plurality of elements, each having a positive electrode (14) and a negative electrode (15) in a liquid electrolyte (S), is disclosed, characterised in that said elements are series connected and in that each element is provided with an aperture (19) communicating with the external liquid environment (E), and in that liquid means (A) for separating the electrolyte and the external liquid environment therebetween, said liquid means consisting of a non-ionised liquid, non-reacting with said electrolyte as well as with said external liquid environment, are provided.

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UNDERWATER BATTERIES PROVIDED WITH LIQUID SEPARATING MEANS BETWEEN INTERNAL ELECTROCHEMICAL ENVIRONMENT AND EXTERNAL LIQUID ENVIRONMENT

DESCRIPTION

The present invention relates to batteries for underwater use provided with liquid means for separating the internal electrochemical environment and the external liquid environment therebetween.

Primary batteries, as well as storage batteries, can be used as power sources in underwater engineering, to operate motors, for lighting, to power-feed electrical apparatuses and the like.

However, at present secondary (storage) batteries, mainly of the lead/sulphuric acid type, and in some instances nickel-iron or nickel-cadmium batteries having an alkaline electrolyte, are widely used.

Currently available storage batteries, both the sealed and the non-sealed ones, have a recess, inside the individual cell units and above the electrolyte, containing air and the gases (hydrogen and oxygen) that can be gradually produced at the electrodes.

Non-sealed batteries have plugs provided with a gas vent. Both battery types, although provided with satisfactorily insulated liquid-tight clips, cannot directly be immersed at sea or lake depths, as salty, brackish or fresh water would enter the non-sealed batteries, entailing the leaking of the electrolyte, whereas sealed batteries would collapse under the external environment pressure. Both instances would entail a voltage drop and a permanent damage of the electrodes, not to mention the relevant environmental damage. Therefore, the state of the art discloses the use of heavy and expensive steel casings, containing, in case of non-sealed batteries, platinum catalysts for hydrogen and oxygen recombination.

In light of the liquid near-incompressibility principle, the subject matter of the present invention is

a system that provides the filling of the recess located above the electrolyte of the cell units of a battery with a liquid meeting specific requisites.

An object of the present invention is that of providing an arrangement for liquid electrolyte batteries allowing the immersion thereof even at great depths, without the occurrence of the above-mentioned drawbacks, up to date solely avoidable by means of costly devices.

According to the present invention, an assembly exploiting the near-incompressibility of the liquids and using a non-ionised liquid separating layer, non-reactive with the battery electrolyte and with the aqueous environment, is provided. The separating layer is arranged in the recess located above the electrolyte solution level in the cell units of the battery, thereby allowing the assembly to be pressurised even at great depths due to the immersion, without introducing significant stresses inside the battery casing.

Other objects, features and advantages of the present invention will be made apparent in the following description, given by way of example and not for limiting purposes, of several presently preferred embodiments thereof and making reference to the Figures of the annexed drawings, wherein:

FIG. 1 is a schematic view of a multiple-cell or element battery provided with liquid separating means (layer) according to the invention and with free apertures, at the top of the individual cell units, communicating with the external liquid environment;

FIG. 2 is a schematic view analogous to that of FIG. 1 and referring to a second embodiment, in which check valves are provided at the apertures at the top of the individual cells or cell units, toward the external liquid environment;

FIG. 3 shows a third embodiment of a battery assembly in which a manifold is provided between the vents of the individual cell units of the battery, the

manifold being provided, at the top portion thereof, with a check valve at an individual aperture communicating with the external liquid environment;

FIG. 4 schematically shows a further embodiment of the battery according to the present invention, in which a multiple-cell battery is housed into a container filled up with the liquid separating means (layer) and the container being provided, at the top portion thereof, with a check valve at an individual aperture communicating with the external liquid environment;

FIGS. 5, 6 and 7 show voltage/time charts for batteries according to the invention under a closed circuit voltage condition.

In light of the aforementioned, and taking into account the Figures of the annexed drawings that will hereinafter be detailed, the object of the present invention is based on the liquid near-incompressibility principle, and it provides a liquid separating layer according to the already outlined conditions.

The liquid separating layer performs the following tasks:

a) it allows the escape of the gases evolved within the battery towards the external environment;

b) it avoids short circuit current between the electrodes of different battery cells.

In the following disclosure the electrolyte solution of the battery will be indicated with S, a liquid floating onto the solution S will be indicated with A, the water of the external environment (sea, lake, etc.) will be indicated with E, and the densities of S, A and E will be indicated with d_S, d_A, d_E, respectively.

Three conditions underlying the present invention are:

1) The density of A must be lower than the density of S, i.e., $d_A < d_S$;

2) A and S must be immiscible therebetween;

3) A and S must be non-reactive therebetween;

When $d_A > d_E$, and always providing the requisites 1-3 are met, the check valve is superfluous and the liquids A and E can be in contact therebetween. In this instance, besides performing the tasks a) and b), the liquid A further performs the following:

c) it prevents the interdiffusion between the solution S and the water E of the external environment;

d) it allows that the internal pressure of each individual cell of the battery be equal to that of the external environment.

It is to be noted that when the batteries according to the present invention use a check valve d_A can be lower or equal to d_E ($d_A \leq d_E$).

The assembly subject matter of the present invention will hereinafter be described with reference to various embodiments thereof. FIGS. 1, 2, 3 and 4 show schematic views of such embodiments, that are to be construed as non-limiting illustrative examples of the invention itself.

FIGS. 1-3 are mere sketches, in which a highlighting of the thickness of the battery casing was omitted. Instead, the latter, as well as the thickness of the container utilised in the fourth embodiment, are highlighted in FIG. 4.

For the device of FIG. 1, in which the liquid A directly contacts the external environment water, i.e., E, a further requirement must be met, precisely:

4) The density of A must be greater than the density of E, hence, taking condition 1) into account, it must be $d_E<d_A<d_S$;

FIG. 1 schematically shows a longitudinal section of the battery according to a first embodiment thereof. Therein, a 6-cell or 6-element assembly, providing a rated voltage equal to 12 V for lead/acid batteries, is shown.

The battery comprises a casing, globally indicated with 10, partitioned into six cell units by partitions 11

extending from the bottom panel 12 of the battery to the top panel 13. Positive and negative plates 14 and 15 are housed within the six cell units, in case spaced apart by known spacers, not shown. The positive and negative plates 14, 15 are interconnected by jumpers 16, sealingly bridging the partitions 11.

The space described by the individual cell units or elements is filled up to a height h_1 with an electrolyte S. In a lead/acid battery the solution S is made of a H_2O/H_2SO_4 solution. In the traditional batteries, the electrolyte S is exposed to air which contains H_2 and is enriched with O_2, the various gas ratios thereof being variable and depending on the operating conditions of the battery, as it is well-known to those skilled in the art.

According to the present invention, on the electrolyte S a liquid separating layer A, of a thickness h_2, non-ionised and non-reactive with the electrolyte S or with the external liquid environment (salty, brackish or fresh water), is located.

The battery is also provided with terminals 17 and 18 for the connection to an electric load (not shown) and, if needed, to a well-known battery recharger. The terminals 17 and 18 are insulated from the external environment, e.g., with silicone or epoxy resins.

At the top portion of each cell unit, elements 19 for communicating the layer A and the external environment E therebetween, comprising an expansion chamber 20 delimited by chokes 21 and 22, are located. The communication elements 19 allow a pressure compensation of the external environment E with the internal environment of the battery S+A.

The presence of the chambers 20 and of the chokes 21 and 22 enables to prevent the external leaking of S+A in case the battery is tilted during the handling or the use.

For the embodiments indicated in FIGS. 2-4, the walls of the battery casing have to be elastic rather

than stiff, in order to adapt to the volumetric changes in the battery content, essentially due to the volumetric changes of S+A at the increase of the external environment pressure. Thus, e.g., 100 atm changes in the external pressure yield volumetric changes lower than 1%, typically of 0.4-0.5%. In fact, liquids are not strictly incompressible, the compressibility value thereof depending on their nature. Hence, different liquids such as E and the S+A complex could have slightly different compressibility, and also the volumetric changes due to such differences are assessable at 0.4-0.5% for pressure changes equal to 100 atm, therefore such as to easily be compensated by the elasticity of the walls of the battery casing. In fact, under such conditions, a cubic battery having a 20 cm corner would undergo linear dimension changes in the order of the millimetre.

In the embodiment of FIG. 1, non-stiff walls are not required for the battery casing, since, according to the Pascal principle, the internal pressure of each individual cell battery equals that of the external environment.

In the construction of the embodiment of FIG. 2, where corresponding elements are indicated with reference numbers equal to those of FIG. 1, check valves V_1, ... V_6, arranged so as to allow the escape of the gases that might evolve from the electrodes 14 and 15 during the battery operation, while preserving the hydrostatic balance among S, A, and E as already indicated, are provided.

In the construction of the embodiment of FIG. 3, in which corresponding elements are indicated with the same reference numbers of FIGS. 2 and 3, the top end of the elements 19 is connected to a manifold pipe network, globally indicated with 23, provided with branches, 24, 25, 26, 27, 28, 29, converging towards a common connection spot 30, at which a check valve VK, having the same purpose of the valves V_1, ... V_6 of FIG. 2, is

arranged. As it is apparent from the drawing of FIG. 3, the arrangement of the various branchings allows the gas produced from the battery to converge to the collection vertex 30.

In the construction of the embodiment of FIG. 4, in which corresponding elements are indicated with the same reference numbers of FIGS. 1, 2 and 3, the casing of the battery 10 is accommodated within a watertight case 31. Said watertight case 31 is provided with a perimetric lip 32 registered with a corresponding perimetric lip 33 onto the bottom portion of an upwards-tapered pyramid-shaped element 34 for collecting the gases evolved at the electrodes 14 and 15 of the various cell units of the battery. At the apex of the pyramid-shaped element 34 a check valve VN is located. At the lips 32 and 33, fastened therebetween with bolts 36, a seal 35 is located.

Within the element 34, seal feedthroughs 37 and 38 for the passage of connection cables to the terminals 17 and 18 of the battery are provided. The entire space around and above the battery casing 10, as well as the space over the electrolyte S is filled up with the separating liquid A, having the already described characteristics and that will hereinafter be better detailed.

Further, it has to be pointed out that the battery housed within the case 31 as shown in FIG. 4 could be replaced by a number of batteries.

The characteristics and the nature of the liquid forming the separating layer A (liquid separating means) between the electrolyte S and the external environment E will hereinafter be disclosed. As above-disclosed, the liquid A must be non-ionised in order to be insulating.

It has to be pointed out that the density of the electrolyte solution of a lead/sulphuric acid battery depends on the battery type and charge. Thus, e.g., the electrolyte density in an electric car battery during the

discharge ranges from 1.33 to 1.21 g/ml, whereas in a battery for stationary plants the density ranges from 1.225 to 1.08 g/ml. In a nickel-iron battery with an alkaline electrolyte (20-30% KOH, 50 g/l LiOH) the density usually exceeds 1.16 g/ml. Therefore, considering that the seawater density is usually lower than 1.025 g/ml, it can be stated that a separating liquid A having a density ranging from 1.04 to 1.07 g/ml, immiscible with aqueous solutions and non-reactive in an acidic or alkaline environment, proves to be an all-purpose separating liquid for storage batteries with an acidic or alkaline electrolyte, to be used according to the embodiment sketched in FIG. 1. However, for any acidic or alkaline electrolyte battery to be used according to the embodiment of FIG. 1, a liquid A, immiscible and non reactive with the electrolyte solution, having a density smaller than the minimum density evidenced by said solution during the discharge process, yet greater than that of the external environment water, can always be found.

Substances useful as separating liquid A, covering the electrolyte solution, in the embodiment of FIG. 1 can be selected also from the following substance classes:

chlorinated hydrocarbons, like, e.g., 1,1,1-trichloroethane, chlorobenzene, 1,1,2,2-tetrachloroethane, 1,2-dichlorobenzene, carbon tetrachloride, trichloroethylene, 2-chlorotoluene, 4-chlorotoluene;

bromidrated hydrocarbons, like, e.g., 1-bromodecane, bromobenzene, 1-bromohexane, bromocyclohexane;

nitroderivatives of hydrocarbons, like, e.g., nitrobenzene;

silicones, like, e.g., the silicone oil 710. These substances can be utilised as such or as mixtures thereof, or even admixed to hydrocarbons. Even solid substances belonging to the first three substance classes like, e.g., solid 1,4-dichlorobenzene, could be dissolved

in other liquid substances of the same class or in hydrocarbons. The solution having the required density can easily be obtained carrying out the admixture of the various substances in presence of a densimeter.

In the embodiments shown in FIGS. 2-4, check valves are provided, preventing the external environment water from entering the battery, as a covering liquid A, besides the substances belonging to the above-mentioned groups, immiscible and non-reactive liquids, the density of which being lower than that of the external environment water, like, e.g., a hydrocarbon mixture like oil, naphtha, kerosene, Nujol or liquid paraffin, (with a density being generally comprised in the range 0.76-0.88 g/ml) or their mixtures can suitably be utilised.

The discharge curves, i.e. the CCV (closed circuit voltage) versus time, of some batteries available on the market modified according to the present invention are shown in FIGS. 5-7. FIG. 5 shows the discharge of a 12V/35Ah lead/sulphuric acid battery, connected to a water-cooled 0.33 ohm/300 W load resistor, the electrolyte solution thereof having been covered according to the embodiment of FIG. 1 with a liquid mixture of several substances belonging to the afore-mentioned groups, by way of demonstration of the compatibility of said substances with the electrolyte.

FIG. 6 shows the discharge of a 1.3V/5Ah nickel-iron battery connected to a 1.74 ohm/4 W load resistor, whereas FIG. 7 shows the discharge of a cadmium-nickel battery, made of seven 1.2V/3Ah cell units, connected to a 12 ohm/20 W load resistor. Both batteries were of the alkaline electrolyte type, and were filled with liquid paraffin according to the embodiments of FIGS. 2 and 4, respectively.

All the above-mentioned curves were obtained with the batteries immersed at a 50 m depth in sea water. Identical discharge curves were obtained for the in-air discharge of the same batteries with the same load

resistors.

CLAIMS

1. A battery for underwater use comprising a plurality of elements, each having a positive electrode and a negative electrode in a liquid electrolyte, characterised in that said elements are series connected and in that each element is provided with an aperture communicating with the external liquid environment, and in that liquid separating means are provided between the electrolyte and the external liquid environment, consisting of a liquid that is non-ionised, insoluble and non-reactive both in respect of said electrolyte and in respect of said external liquid environment.

2. The battery according to claim 1, characterised in that said elements are made of cell units and in that said liquid separating means have a density intermediate between that of said electrolyte and that of the external liquid means, made of fresh or salty water.

3. The battery according to claim 1 or 2, characterised in that at the top of each element or cell unit an aperture communicating with the external liquid environment is provided in order to allow a hydrostatic pressure balancing between the interior and the exterior of the battery, said aperture being chamber-shaped and vented at the top thereof, and with one or more narrow openings in order to avoid the leaking toward the external environment of the liquid separating means and of the electrolyte when said battery is tilted.

4. The battery according to one or more of the claims 1 to 3, characterised in that said apertures at the top of each element or cell unit are connected to a manifold having an individual aperture in correspondence of the external environment.

5. The battery according to one or more of the preceding claims, characterised in that it comprises a secondary casing housing said battery, wherein the space between the battery and said casing is filled up with said liquid separating means and it is provided with an

individual aperture communicating with the external environment, there being also provided insulated and liquid-tight thorough-leads for connecting said battery to an electric load or to a battery recharger.

6. The battery according to one or more of the preceding claims, characterised in that said liquid separating means which are non-ionised and non-reactive with the electrolyte of the battery and with the external liquid environment and have an intermediate density between that of the battery electrolyte and that of the external liquid environment, consisting of fresh or salt water, are selected from one or more of the following substance classes:

chlorinated hydrocarbons, like, e.g., 1,1,1-trichloroethane, chlorobenzene, 1,1,2,2-tetrachloroethane, 1,2-dichlorobenzene, carbon tetrachloride, trichloroethylene, 2-chlorotoluene, 4-chlorotoluene;

bromidrated hydrocarbons, like, e.g., 1-bromodecane, bromobenzene, 1-bromohexane, bromocyclohexane;

nitroderivatives of hydrocarbons, like, e.g., nitrobenzene;

silicones, like, e.g., the silicone oil 710.

7. The battery according to claim 1, characterised in that said elements are made of cell units and in that said liquid separating means have a density that is lower than that of the electrolyte, and in that at the top of each element or cell unit a check valve is provided, arranged so as to allow the escape of gases produced during the operation of the battery and to prevent the entering of the external liquid environment.

8. The battery according to claim 7, characterised in that said apertures at the top of each element or cell unit are connected to a manifold having a individual check valve.

9. The battery according to claim 7 and/or 8 characterised in that said liquid separating means have a

density that is lower than that of the electrolyte and also of the external liquid environment and consist of oil, naphtha, kerosene, mineral oil (Nujol), liquid paraffin and mixtures thereof.

10. The battery according to one or more of the preceding claims, characterised in that said elements or cell units are of the lead/sulphoric acid type or the nickel-iron or nickel-cadmium type.

11. The battery according to one or more of the preceding claims, characterised in that, in the assemblies provided with check valves, the casing of the battery and/or said secondary casing are made of a relatively yielding material, in order to compensate the different compressibility between the external liquid means and the complex electrolyte/separating liquid.

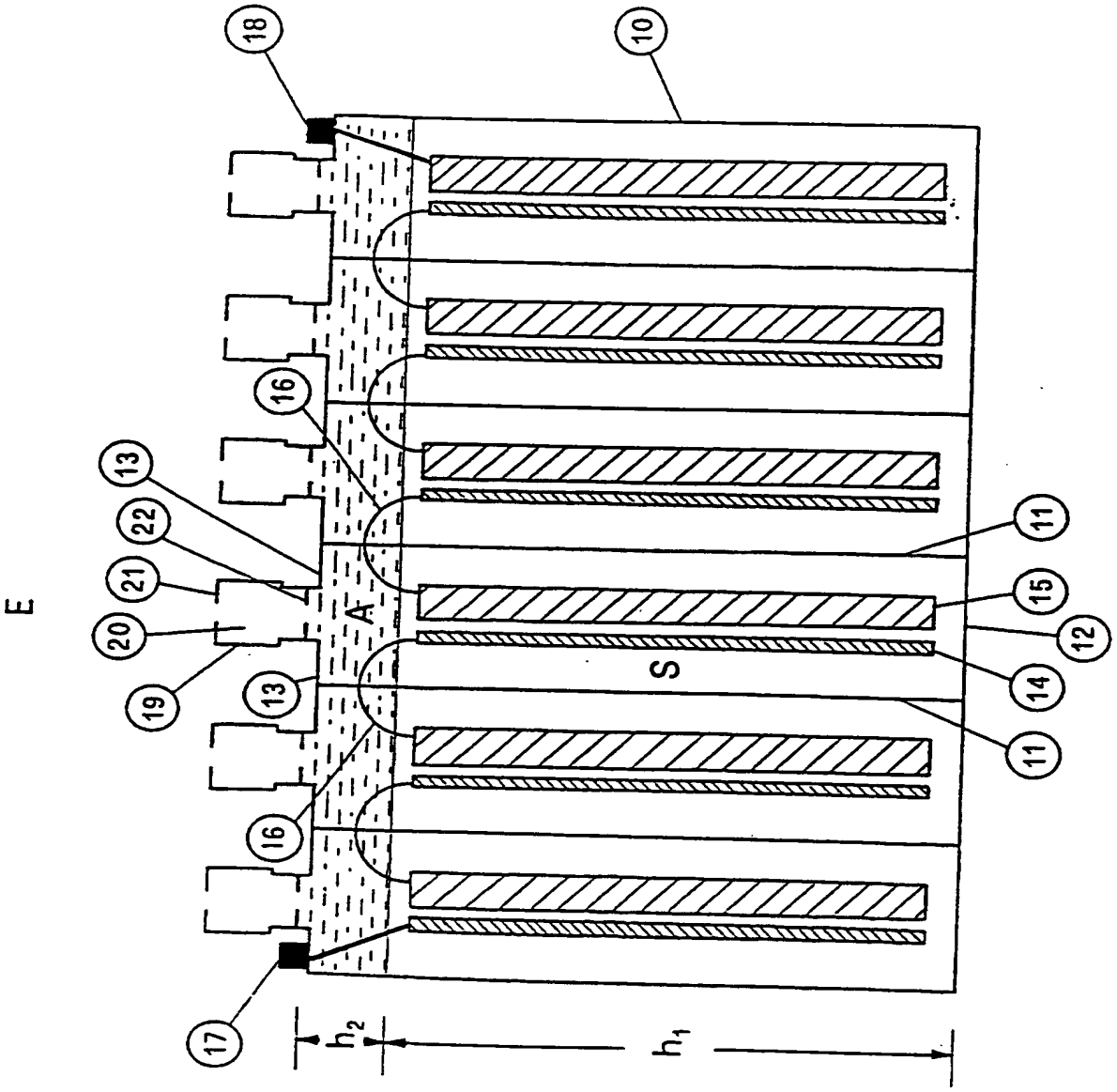


FIG. 1

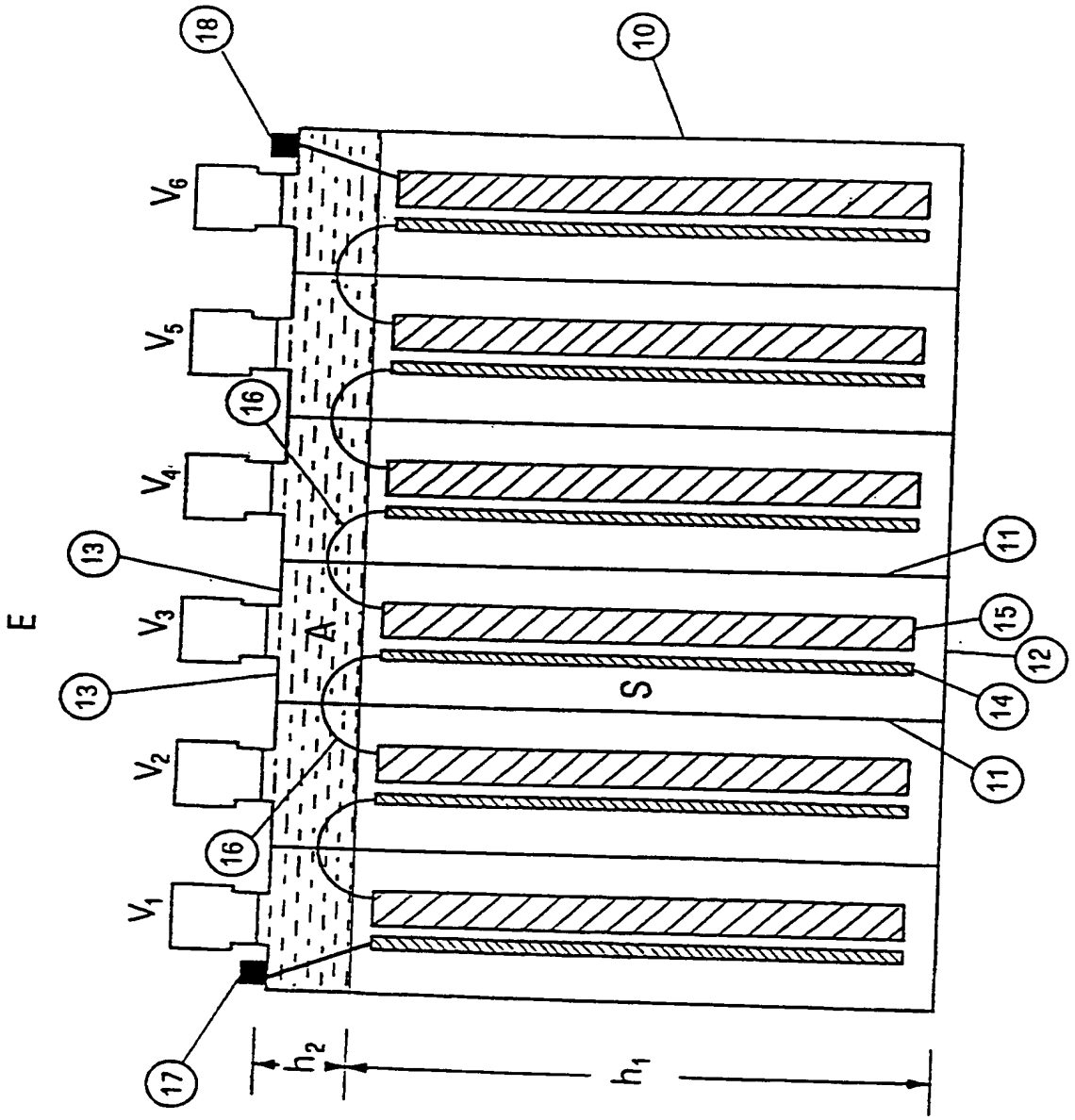


FIG. 2

FIG. 3

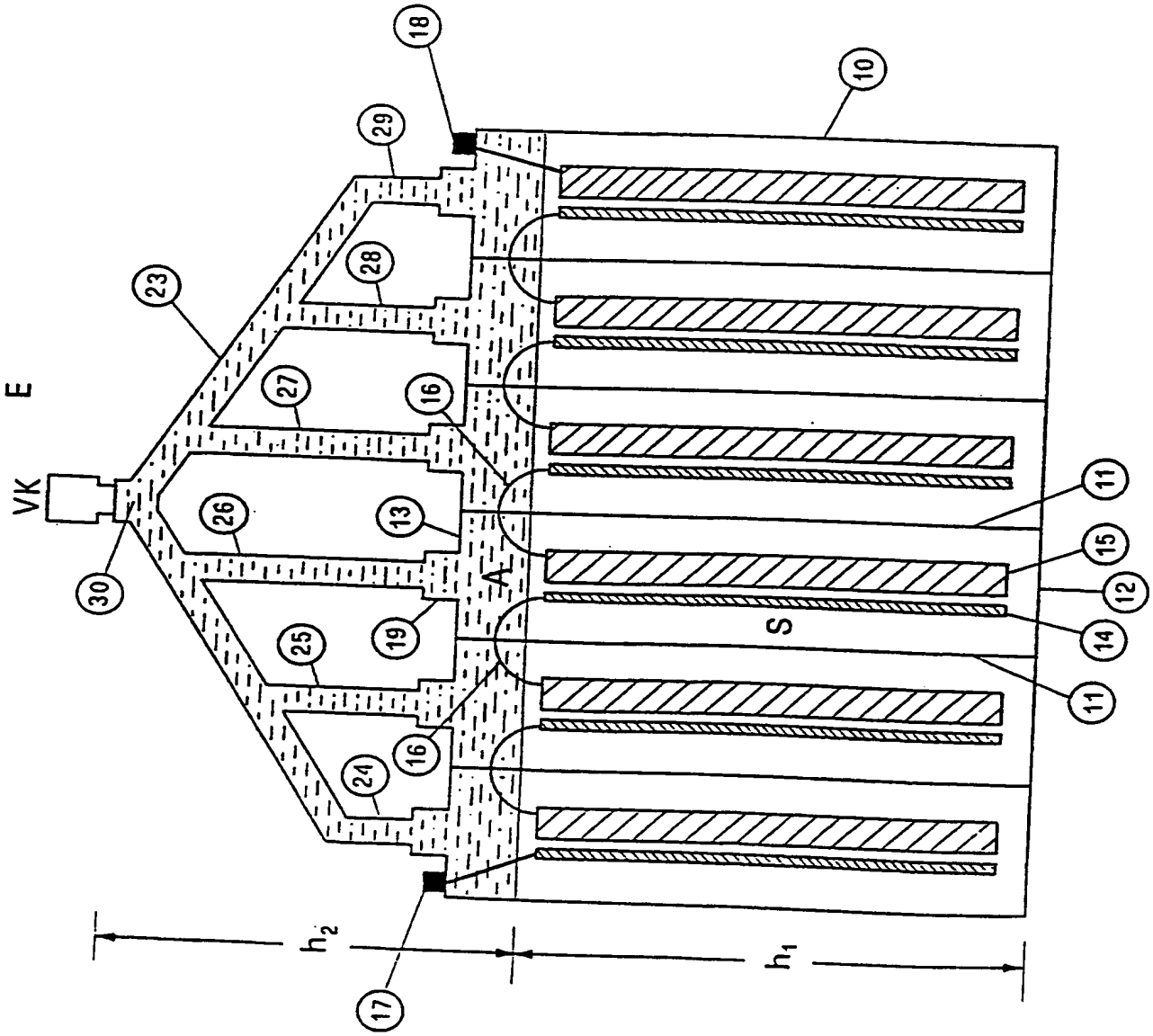
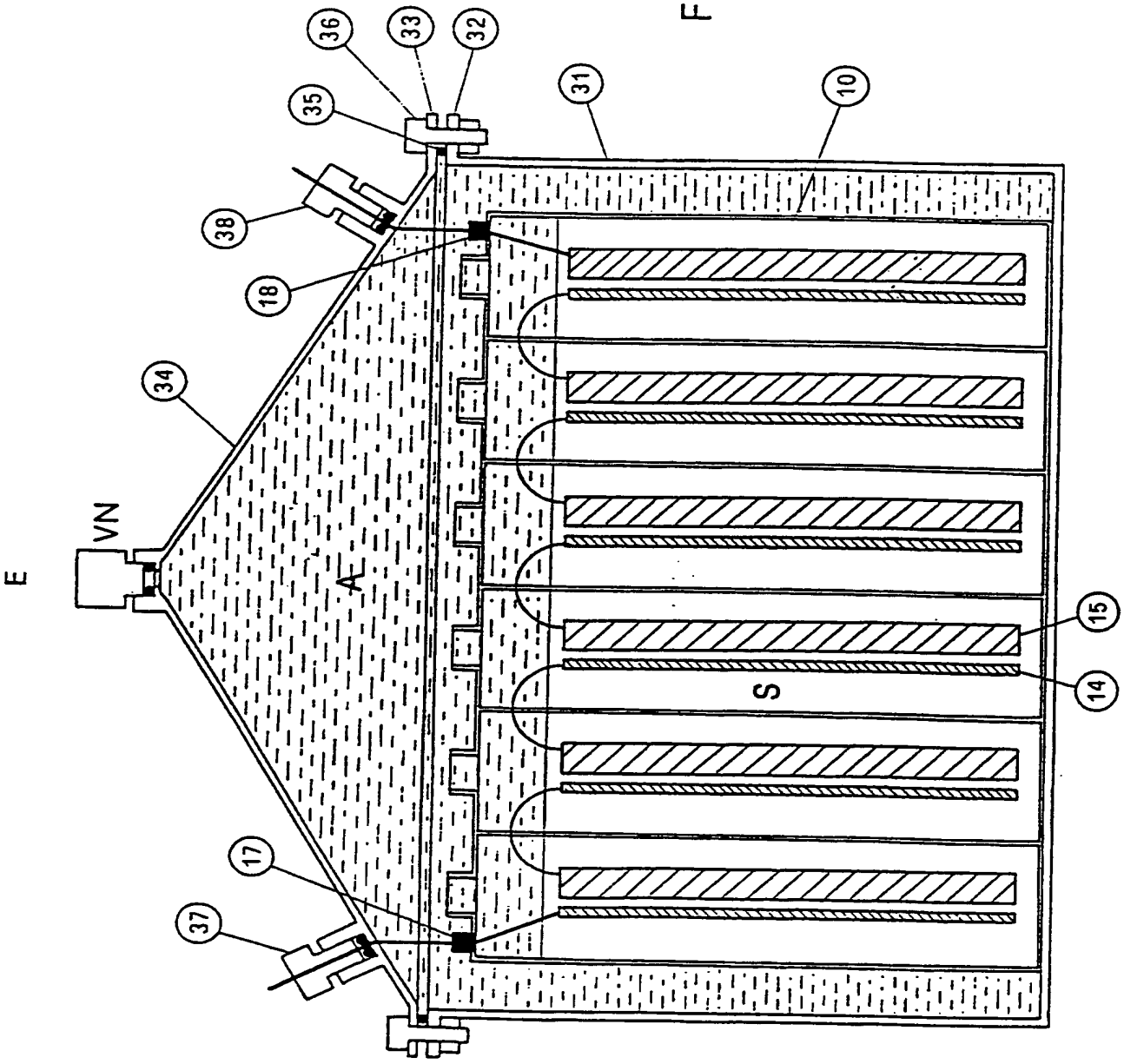


FIG. 4



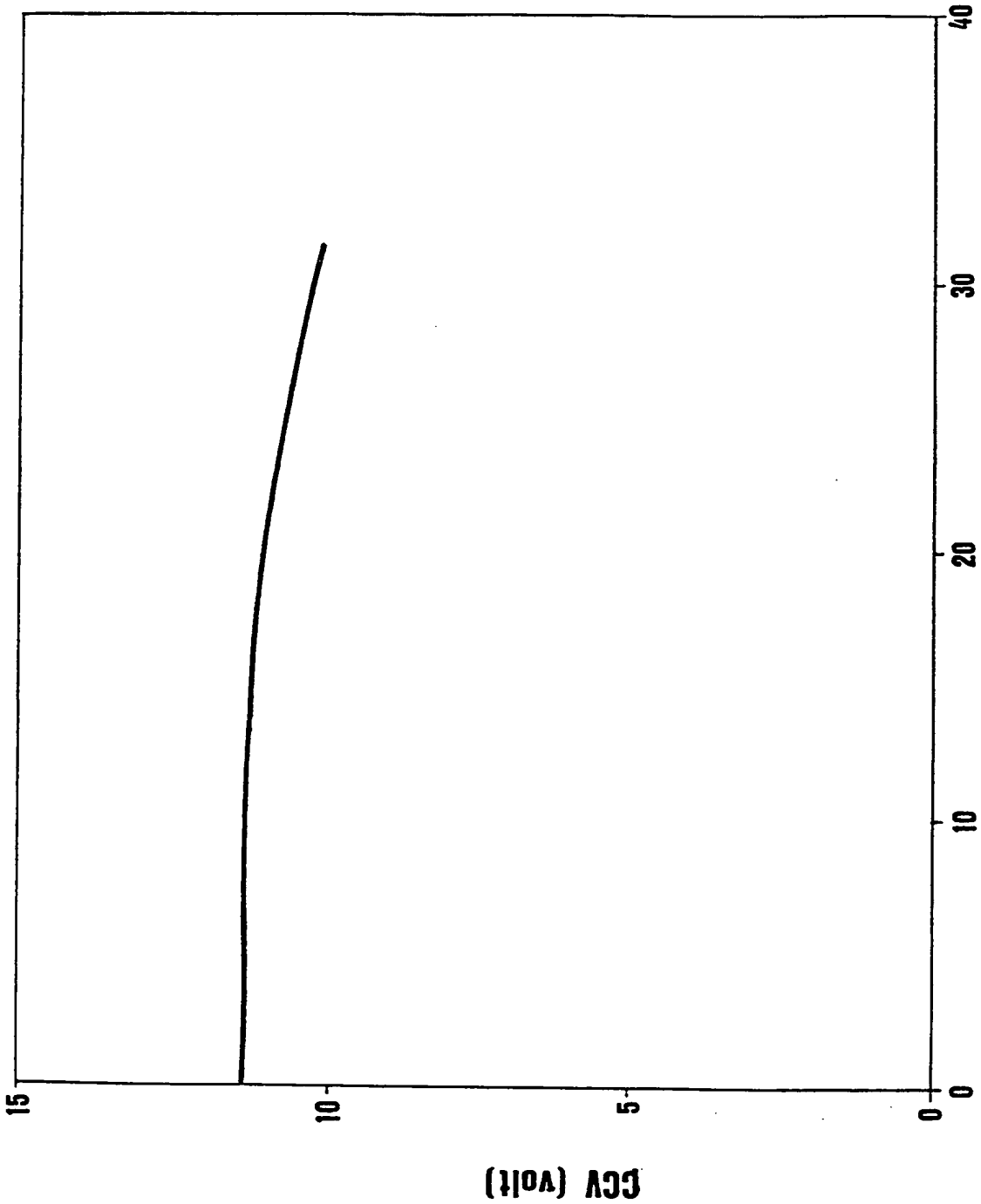


FIG.5

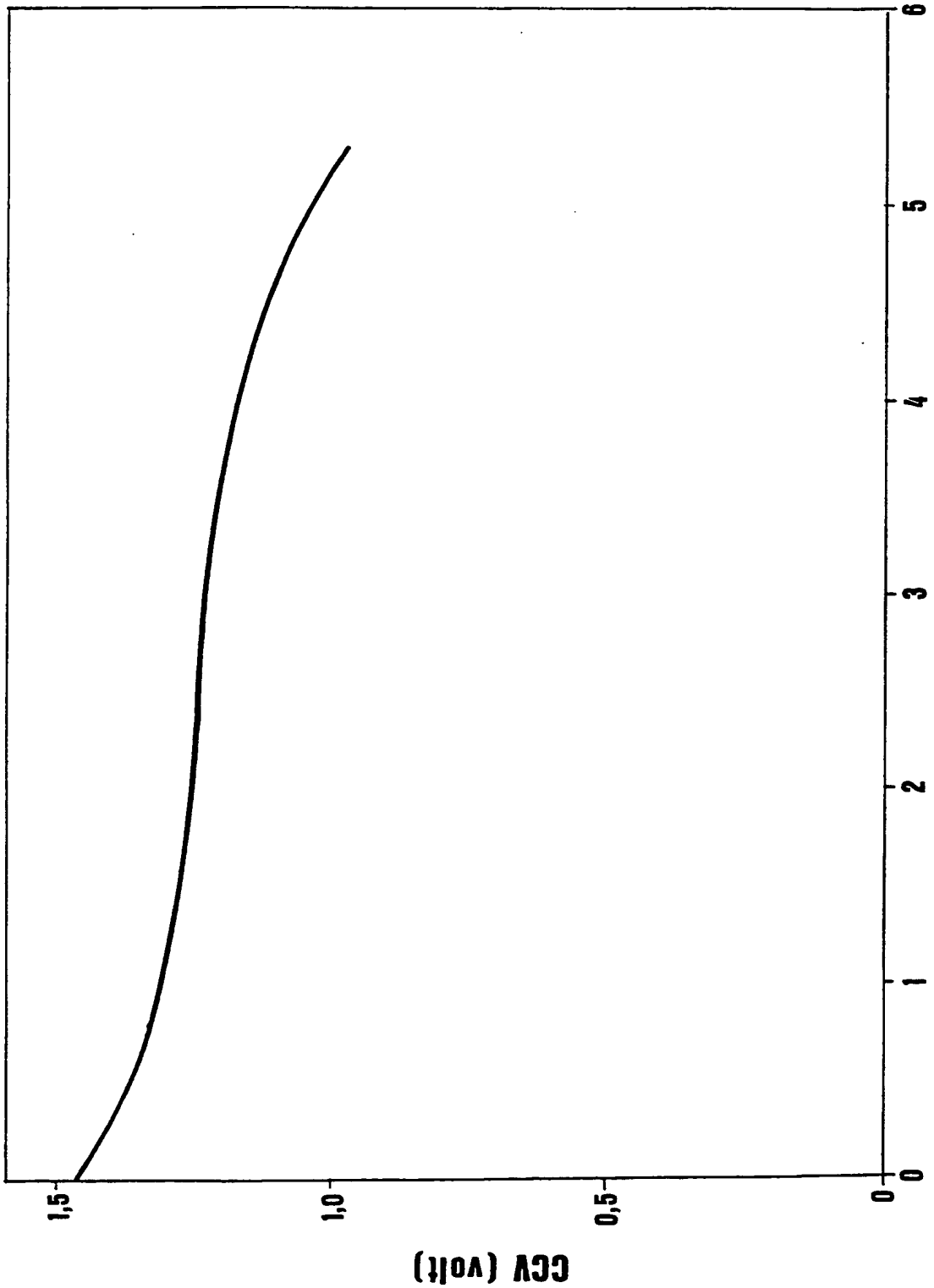


FIG.6

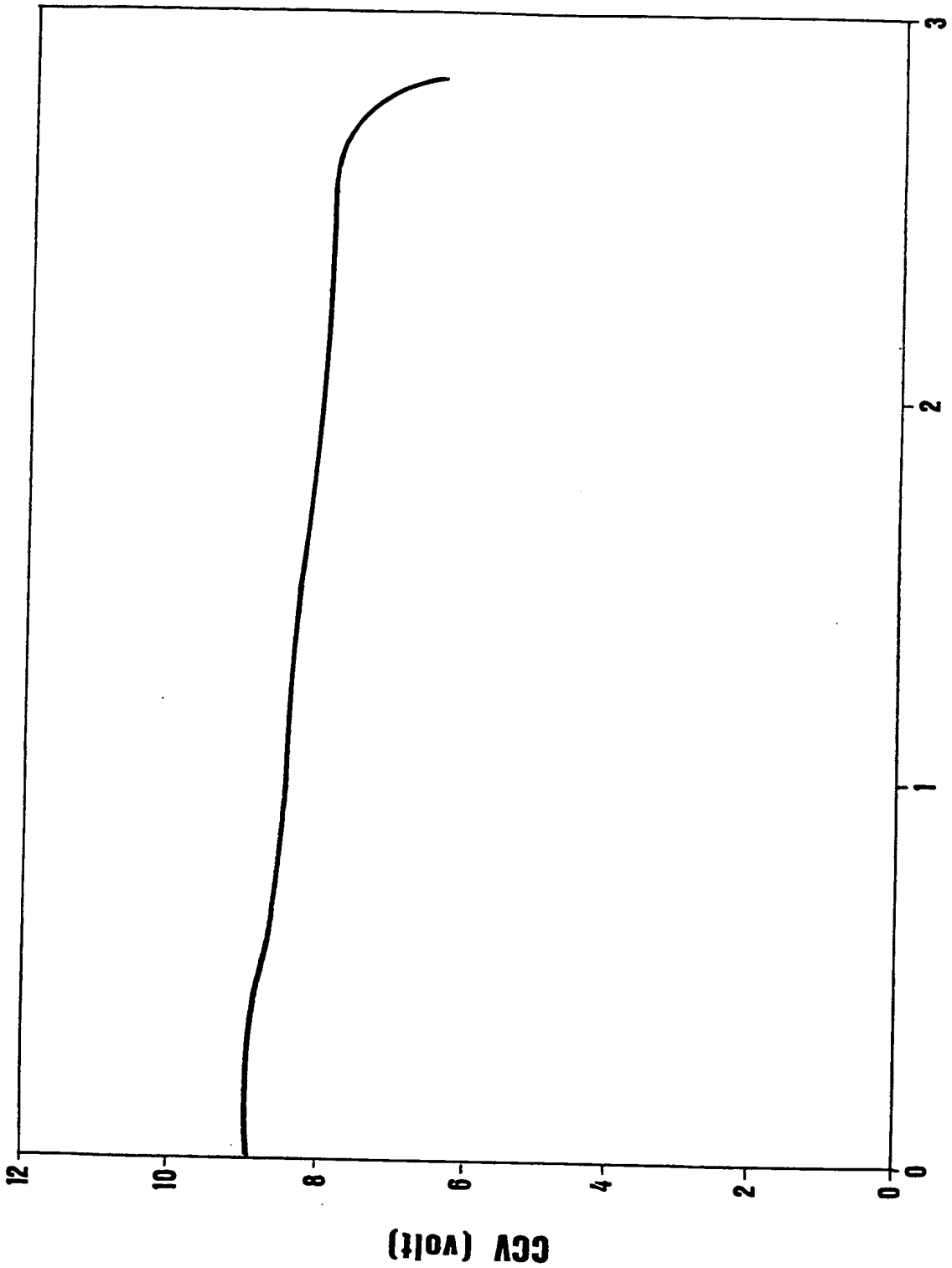


FIG.7